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IN SPECIMENS MADE FROM POLYOLEFINS AND POLYSTYRENE

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ON THE DISTRIBUTION AND MIGRATION OF ANTISTATIC AGENTS  
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Summary

In injection-molded sheets made of polyolefins and impact-resistant polystyrene containing anionic antistatic agents (lithium salts of carboxymethylated ethoxylates as well as alkane sulfonic acids and alkyl benzene sulfonic acids), equilibrium existed immediately after the molding operation between the molecules of the antistatic agents on the surface and those inside the molded objects. In other words, the thickness of the surface layer did not change to any considerable extent during several weeks of storage. The thickness depended on the type of polymer and on the type and concentration of the antistatic agent used. If glycerol was used, it increased considerably, by two to twenty-one fold, depending on the polymer and antistatic agent used as well as on the concentration of the antistatic agent and of the glycerol. This is attributed to an increase in the rate of diffusion of the antistatic agent due to the presence of glycerol. From the results of discontinuous surface washing tests it was concluded that below the polymer surface of injection-molded objects there is a minimum in the concentration of the antistatic agent, which fills up during extended storage of the test samples.

The diffusion coefficients for the antistatic agents obtained from continuous extraction are in proper relation to the surface layer thickness.

## 1. Introduction

There are two ways of preventing electrical charges on the surfaces of polymers with surface-active substances (tensides): external application by spraying, dipping, etc., and internal application by homogeneously mixing the antistatic agent with the polymers. Although part of the antistatic agent applied externally migrates into the interior of the part [1], the surface coating is mostly removed by wiping or washing the polymers. This disadvantage is avoided with internal application. Here, those antistatic agents having limited incompatibility with the polymers should be used. In the ideal case a thin layer forms on the surface. The concentration of antistatic agent in this layer is considerably greater than in the interior of the polymer. If the surface layer is in some manner removed from plastics treated in this way, enough of the antistatic agent can migrate from the interior to produce a new surface layer. The thickness of the layer, the rate at which this layer develops after forming, or develops again after a surface layer has been removed, and the electrical conductivity of the layer are important criteria for the quality of an antistatic agent. The analytical determination of these criteria is, then, of general interest for antistatic application.

A large number of methods is already known, which were prepared for determination of the concentration of surface-active substances on the surface of plastic specimens and in regions near the surface. For instance, both regions can be determined by removing the surface with KBr [2] or steel wool [3]. The uncertainty about the thickness of the removed layer can make these methods too inaccurate. The fact that the thickness of the layer being analyzed cannot be determined accurately is also a disadvantage in determination of the surface layer using FMIR (multiple reflection infrared) spectroscopy [4, 5]. This method also depends on a characteristic infrared spectrum of the substance to be determined, which must not be perturbed either by the

polymer or by other additives (plasticizers, lubricants, etc.), so that this method is certainly limited to special cases.

Certainly the methods which appear most elegant are those in which radioactively labeled compounds are worked into the polymer. Then they are determined, by their radioactivity, in solutions obtained by periodic washing of the additive from the surface [6] or through continuous extraction [7-10]. Amounts of substances migrating from one polymer sheet into another are also determined in the same way [11]. Of course, availability of an isotope laboratory is a prerequisite for this method.

Other authors describe contact angle measurements of water drops on the surface of specimens [12, 13] or measurement of the specific surface tension in solutions obtained by extraction [1, 14]. These two methods were not generally applicable for us because for the most part we use mixtures of antistatic agents with other substances. The different distribution or migration of the components of a mixture prevents analyzing them separately. The same reason eliminated the electrical surface resistance [1] also as a measure for the surface concentration for us.

For our experiments, we selected lithium salts of surface-active carboxylic acids and sulfonic acids because lithium can be determined very accurately by flame photometry. The lithium salts have the advantage over the sodium and potassium salts that error in the analytical results from environmental contaminants is expected only to a very minor extent.

## 2. Performance of the Experiments

### 2.1 Starting Materials

We used high-density polyethylene (Vestolen A 6016 and Vestolen A 5017), polypropylene (Vestolen P 5500) and Polybutene-(1) (Vestolen BT 8000) (products of Vestolen, Inc., Marl). For

polystyrene we used the impact-resistant type Vestyron 512, a polymer from the Chemische Werke Hüls, Inc.

As internal antistatic agents we used:

- a) a mixture of 77% O-carboxymethylated fatty alcohol oxyethylates with the formula  $R-O-(C_2H_4O)_n-CH_2COOLi$  and 23% fatty alcohol oxyethylates with the formula  $R-O-(C_2H_4O)_n-H$ , with  $R = C_{12}H_{25}$  and  $C_{14}H_{29}$ , and with  $n \approx 4.5$ . This is designated in the following as Li-BW 1072, after the product in the acid form, "BW 1072" of Chemische Werke Hüls AG.
- b) lithium alkanesulfonate,  $R-SO_3-Li$  with  $R = C_{15}H_{31}$  and  $C_{16}H_{33}$ , designated in the following as Li-K30 (according to the corresponding sodium salt, "Emulgator K30" of Bayer AG).
- c) Lithium alkylbenzenesulfonate,  $R-C_6H_4-SO_3-Li$ ;  $R = C_{11}H_{23}$ , designated in the following as Li-Marlon A (according to the corresponding sodium salt, "Marlon A" of Chemische Werke Hüls AG).

The lithium salts were obtained by converting the free acids with LiOH. The free acids, if not otherwise accessible, were obtained from the sodium salts by means of cation exchangers.

## 2.2 Production of the Test Specimens

The additives were mixed into polyolefin powder. The mixtures were compressed in the extruder, and the extrudate was ground. Sheets measuring 80 x 65 x 1 mm were made by injection molding from the granulates obtained. In order to prepare the polystyrene granulates, the additives were mixed in during the block polymerization of the styrene-rubber mixture.

## 2.3 Removal of the Surface Film and Determination of the Lithium Content

Eight injection-molded plates were shaken in a glass tray with completely desalted water. Pieces of wire were placed between the individual plates to maintain adequate separation.

As only half of a plate was washed with water in this washing process, the plates were turned over and treated in the same manner as before.

In most cases, more than eight plates (up to 64) were treated in the same water so as to increase the analytical accuracy through higher lithium concentration. The washing time was 20 seconds in the normal case. The solutions obtained were mixed with sulfuric acid and evaporated to fumes. The residues were dissolved in water and the lithium contents were determined by flame photometry.

## 2.4 Measurement of the Electrical Surface Resistance

The electrical surface resistances of the plates were measured with a Tera-Ohmmeter from the R. Jahre Company, Berlin, according to DIN 53482 (departing from the standard by using 60% relative humidity).

## 3. Evaluation of the Measurements

### 3.1 Correction of the Analytical Values for the Amount of Extraction

Within the time period in which the plate surface is covered by water in the washing process, there is not only removal from the surface, but already some extration from the interior of the sheet. In order to eliminate this extraction from the interior of the made use of a graphical method, that of W. Biedermann [14].

Differences in the lithium values every 5 seconds were plotted versus the total removal time. By extrapolating both branches of the curve inward, we obtained at the point of intersection the amount of lithium,  $m_K$ , which was extracted from the interior of the plate in 5 seconds (see Figure 5 for the schematic presentation). For a washing period of 20 seconds, then, we subtracted from the

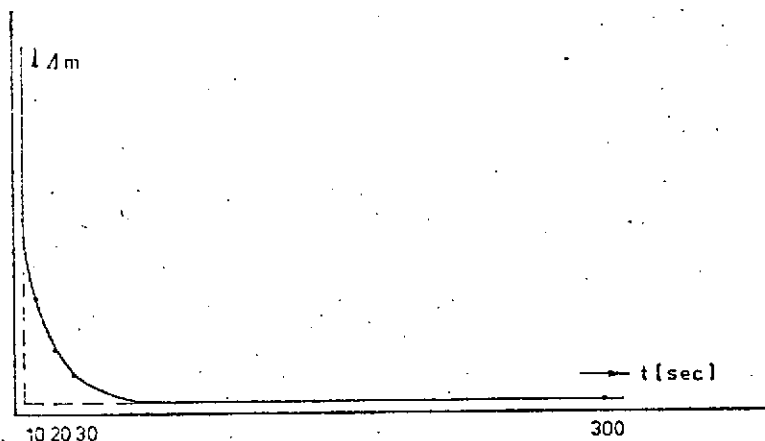


Figure 1. The amount of lithium taken up by the water within each period of 5 seconds (schematic representation).

amount of lithium determined analytically,  $m_A$ , the amount of lithium which was extracted during this period, or  $4m_K$ . The corrected value then is  $m = m_A - 4m_K$ . For all the formulations studied, the value of  $m_K$  is of the order of 0.6% of  $m_A$ .

### 3.2 Calculation of the Degree of Coverage

The degree of coverage, i. e., the number of molecular layers on the surface, was calculated from  $m$ . The degree of coverage on untreated plates is designated as the "first degree of coverage",  $n_E$ .

The percentage  $m_g$ , referred to the total amount incorporated, is also calculated. Because of the different amount of Li in the individual salts,  $m_g$  is different from one formulation to another. For calculation of  $n_E$  we proceeded on the simplifying assumption that the plates are completely flat and that the space requirement (according to W. Biedermann [14]) for an oriented surface-active molecule is  $F = 16 \text{ \AA}^2$ . Then the

number of molecules on the sheet surface,  $F$ , with monomolecular coverage would amount to  $x_1 = F/F'$ . The total number of molecules on the surface,  $x_g$ , is determined from  $m = m_A - 4m_K$ , the Loschmidt number,  $N_L$  ( $6.023 \cdot 10^{23}$ ) and the atomic mass of lithium,  $M_{Li}$  ( $6.939 \cdot 10^6 \mu g$ ):

$$x_g = \frac{(m_A - 4 m_K) \cdot N_L}{M_{Li}}. \quad \text{Then the number of molecular layers (degree of coverage) is } n = \frac{x_g}{x_1} = \frac{(m_A - 4 m_K) \cdot N_L \cdot F'}{M_{Li} \cdot F}.$$

#### 4. Results and Discussion

##### 4.1 Results with Polymer-Antistatic Agent Mixtures

Groups of 24 fresh sheets were shaken in water for 20 seconds immediately after production and at definite intervals thereafter. The lithium content,  $m_A$ , was determined in the solutions obtained. The corrected values,  $m$ , were recalculated to get the first degree of coating,  $n_E$  (Table 1). Also, the percentage of the surface coating was calculated from the total amount of the additive. Finally, the matching electrical surface resistances  $[M\Omega]$  are shown in Table 1.

From Table 1 we can see the following:

- a) Even immediately after production of the plates, the specimen is coated with a layer of antistatic agent which becomes only slightly greater in the course of some weeks, independent of the nature of the additive. That is, there is from the beginning an equilibrium between the antistatic agent on the surface and in the interior <sup>1</sup>.

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<sup>1</sup> Similar results were also described by H. Marumo with calcium salts of amphoteric compounds of the imidazoline type [3].



Table 1. FIRST DEGREE OF COATING,  $n_E$ , PERCENTAGE OF  $n_E$  IN THE TOTAL AMOUNT OF ADDITIVE,  $m_g$ , AND ELECTRICAL SURFACE RESISTANCE,  $R_o$

Additive [parts (T) per hundred parts of polymer, by weight]	Vestolen A 6016					
	$n_E$ immediately after production	% of the additive	$n_E$ one day after production	$R_o$ [MΩ]	$n_E$ 7 days after production	$n_E$ 14 days after production
1T. Li-BW 1072	0,09	0,010	0,10	$> 10^7$	0,11	0,14
1T. Li-K30	0,13	0,010	0,15	$> 10^7$	0,15	
1T. Li-Marlon A	0,13	0,012	0,15	$> 10^7$	0,15	

	Vestolen P 5500				Vestolen BT 8000		
	$n_E$ one day after production	% of the additive	$R_o$ [MΩ]	$n_E$ 32 days after production	$n_E$ one day after production	% of the additive	$R_o$ [MΩ]
1T. Li-BW 1072	0,05	0,006	$> 10^7$	0,05	0,05	0,006	$> 10^7$
1T. Li-K30	0,20	0,015	$> 10^7$	0,20	0,13	0,010	$> 10^7$
2T. Li-K30	0,39	0,028	$8 \cdot 10^6$	0,45	0,43	0,037	$> 10^7$
1T. Li-Marlon A	0,16	0,015	$> 10^7$	0,13	0,20	0,018	$> 10^7$
2T. Li-Marlon A	0,46	0,043	$8 \cdot 10^5$	0,50	0,49	0,045	$1 \cdot 10^6$

Table 1, Continued.

Additive	Vestyron 512					
	$n_E$ one day after production	% of the additive	$R_o$ [MΩ]	$n_E$ 15 days after production	49 days after production	116 days
2T. Li-K30	1,30	0,094	$6 \cdot 10^3$	1,41	1,33	1,53

b) The first degree of coating,  $n_E$ , is 0.05 to 0.09 for all polyolefins with 1 part per hundred Li-BW 1072, and 0.13 to 0.20 molecular layers for both the other two lithium salts; that is, it is 0.006 to 0.01 and 0.01 to 0.015%, respectively, of the total additive.

c) When the content of lithium salt is doubled (to 2 parts per hundred),  $n_E$  also rises by a factor of 2 to 4.

d) If only about 0.3 or less molecular layers are present on the surface, the electrical surface resistance is above  $10^7$   $\Omega$ . Only with more than 0.3 molecular layers does  $R_o$  decrease below  $10^7$   $\Omega$ . This is true for all three salts.

#### 4.2 Results with Polymer-Antistatic Agent Mixtures Modified by Addition of Glycerin

As can be seen from the previous section (Table 1), the amounts of lithium found were very small in spite of the use of 24 sheets in common washing. The analytical errors were correspondingly large. In order not to have to increase the sheet number even more, we referred back to a method which prescribes the additional use of glycerin to increase the antistatic action of fatty acid monoglycerides [15, 16]. We expected that the use of glycerin would not only increase the surface conductivity through its hygroscopic effect, but, as an aid to diffusion, would also increase the amount of the antistatic agent on the surface of the specimens.

In the literature, to be sure, glycerin has several times been mentioned as an antistatic agent in itself [17, 18], otherwise as a source of humidity [19-25], or as a co-antistatic used externally [26] together with organic ammonium compounds [27], ethoxylated amines [28, 29], polysiloxanes [30], fatty acid esters [31], polyglycol ethers and organic sulfates

phosphates [32], or used internally together with amines and ammonium compounds [33, 34], cyanoethyl and carbamoyl derivatives of alkanol ethoxylates [35], salts of fatty acids [36, 37], and organic phosphates [33, 38]. Yet either nothing at all has been said about the nature and mechanism and extent of the action of glycerin, or these have been attributed to its hygroscopicity. Only in the case of viscose sheet with a content of 15% glycerin as a plasticizer was it established that glycerin promotes the diffusion of gases ( $O_2$ ,  $N_2$ ,  $CO_2$ ) [39, 40].

Now the first degree of coating,  $n_E$ , and the surface resistance,  $R_o$ , of polymer-antistatic agent mixtures additionally containing glycerin were determined. The results are in Table 2.

With the glycerin-containing mixtures also, a state of equilibrium arises during production of the injection-molded sheets, and practically remains unchanged during storage thereafter. By comparing Table 1 and Table 2, furthermore, we can establish that the surface coating of antistatic agent is considerably increased for preparations containing glycerin in comparison to those without glycerin. The magnitude of this increase depends on the nature of the polymer, the nature of the antistatic agent, and the amount of glycerin (Table 3).

As with the glycerin-free formulations, so too with those containing glycerin, a certain surface resistance ( $R_o$ ) appears at a certain degree of covering ( $n_E$ ). If  $n_E$  exceeds one,  $R_o$  goes below the  $10^4$  MΩ limit. This is true for all the additives and polymers studied. This shows that glycerin exerts a diffusion-promoting effect on certain antistatic agents.

In the literature, very little has yet been reported about substances which promote the diffusion of surface-active substances in polymers. In polystyrene, these are hydroabiethylalcohol [41-43], esters of triethylene glycol and

Table 2. FIRST DEGREE OF COATING  $n_E$ , PERCENTAGE OF  $n_E$  IN THE TOTAL AMOUNT OF ADDITIVE, AND ELECTRICAL SURFACE RESISTANCE,  $R_o$ , IN THE PRESENCE OF GLYCERIN (G1).

Additive	Vestolen A 6016							
	$n_E$	% of	$n_E$	$R_o$	$n_E$			
	immediately after production	the additive	one day after production	[MΩ]	7 days after production	14 days after production	21 days after production	49 days after production
1 T. Li-BW 1072 + 1 T. Gl.	0,60	0,069	0,62	$9 \cdot 10^4$	0,72	0,84		
1 T. Li-K30 + 1 T. Gl.	1,52	0,110	1,50	$4 \cdot 10^3$	1,50	1,40	1,55	1,85
1 T. Li-K30 + 2 T. Gl.	2,73	0,209	2,65	$1 \cdot 10^3$				
1 T. Li-Marlon A + 1 T. Gl.	1,03	0,086	0,99	$1 \cdot 10^4$	1,05	1,01	1,09	1,19

	Vestolen P 5500			Vestolen BT 8000			
	$n_E$	% of	$R_o$	$n_E$	$n_E$	% of	$R_o$
	one day after production	the additive	[MΩ]	32 days after production	one day after production	the additive	[MΩ]
1 T. Li-BW 1072 + 1 T. Gl.	0,20	0,023	$> 10^7$	0,20	0,13	0,015	$> 10^7$
1 T. Li-K30 + 1 T. Gl.	0,44	0,032	$5 \cdot 10^6$	0,65	0,26	0,020	$> 10^7$
2 T. Li-K30 + 1 T. Gl.	1,50	0,115	$6 \cdot 10^3$	1,48	2,80	0,204	$2 \cdot 10^3$
1 T. Li-Marlon A + 1 T. Gl.	0,44	0,041	$3 \cdot 10^6$	0,59	0,31	0,029	$> 10^7$
2 T. Li-Marlon A + 1 T. Gl.	2,44	0,227	$1 \cdot 10^3$	2,60	3,12	0,290	$1 \cdot 10^3$

Table 2, Continued.

Additive	Vestyron 512					
	$n_E$	% of the additive	$R_o$ [M2]	$n_E$		
	one day after production			15 days after production	49 days after production	116 days
2 T. Li-K30 + 1,5 T. Gl.	2,40	0,175	$1 \cdot 10^3$	2,51	2,72	3,11

Table 3. INCREASE IN THE SURFACE COATING,  $n_E$ , BY THE FACTOR F THROUGH ADDITIONAL USE OF GLYCERIN (Gl).

Antistatic agent/ glycerin	Factor F for			
	Vestolen A 6016	Vestolen P 5500	Vestolen BT 8000	Vestylon 512
1 T. Li-BW 1072/1 T. Gl.	6,7	4,0	2,6	
1 T. Li-K30 /1 T. Gl.	11,5	2,2	2,0	
2 T. Li-K30 /1 T. Gl.		4,1	8,5	1,8 (1,5 T. Gl.)
1 T. Li-K30 /2 T. Gl.	21,0			
1 T. Li-Marlon A/1 T. Gl.	7,9	2,7	1,6	
2 T. Li-Marlon A/1 T. Gl.		4,4	6,4	

T: parts per hundred parts, by weight.

and caprylic acid [42, 43] and dibutyl sebacate [1]. In part, they are also called drawing agents.

#### 4.3 Distribution of the Antistatic Agent in the Interior of the Specimen

The following experiments are concerned with the possibility of drawing conclusions about the distribution of the antistatic agent in the interior of the injection-molded sheets by periodically washing off the surface coating. To do this, the sheets were washed with water for 20 seconds immediately after production and then at the intervals 1-1-1-1-(3-2-2)<sub>n</sub> days. Such "washoff series" were also performed with identically formulated sheets which had been stored for 2 or 3 weeks before the beginning of the first washing. The formulations 1 part Li-K 30 + 1 part glycerin and 1 part Li-Marlon A + 1 part glycerin in two different batches of Vestolen A 6016 were used. The averages of the amounts of lithium removed (from the two parallel experiments) are plotted, versus the time after production, in Figures 2 and 3.

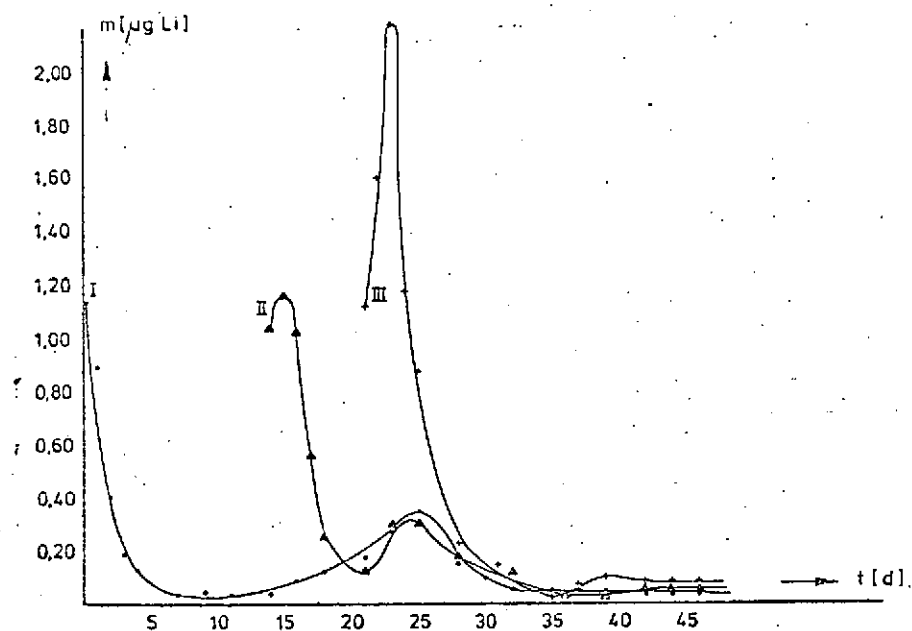


Figure 2. Amount of lithium removed, referred to 1 day and 1 plate (1 part Li-K 30 + 1 part glycerin).

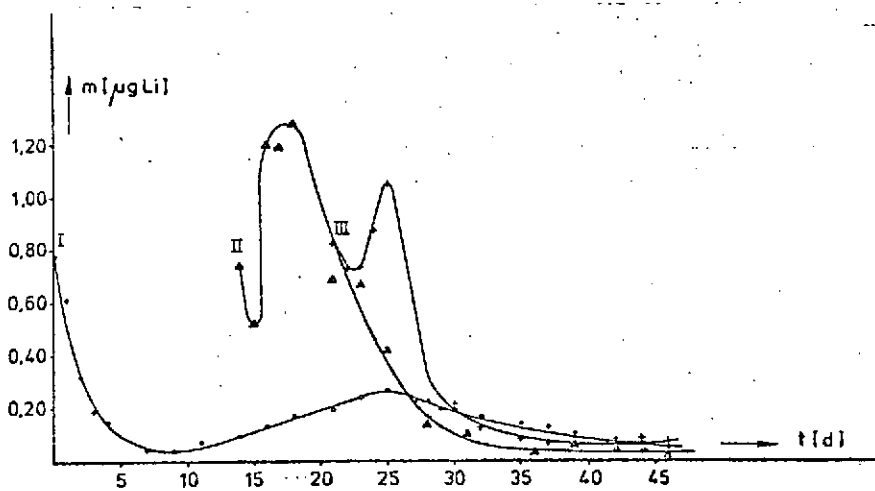


Figure 3. Amount of lithium removed, referred to 1 day and 1 plate (1 part Li-Marlon A + 1 part glycerin).



The amounts of lithium washed off drop sharply in the first days in Curves I of Figures 2 and 3. This cannot be an effect of the migration rate of the antistatic agent alone because later, larger amounts of lithium can be washed off again. The decrease must, in our opinion, also be the result of a reduced concentration of antistatic agent under the sheet surface. Such a concentration minimum has already been demonstrated by Marumo [3] in polyethylene films containing calcium salts of amphoteric compounds of the imidazoline type.

But this minimum in the antistatic agent concentration is observed only if the washoff series is started immediately after production of the plates. As Curves II and III of Figures 2 and 3 (storage for 2 or 3 weeks, respectively) show, the minimum fills in because of antistatic agent migrating back. The amounts of lithium initially washed off are considerably greater than for the curves I.

#### 4.4 Migration of the Antistatic Agents

It was also of interest to establish the rate at which the antistatic agents migrate in polymers. A method is described in the literature [44] for substances of similar molecular weight. The method determines the migration by means of diffusion equations, through continuous extraction with water.

This method was used, except for the calculation procedure. Sets of 10 plates in the 65 x 40 x 1 mm format were shaken continuously with 70 ml of completely desalted water. After certain times, the lithium content in the water was determined, and the extraction was continued with fresh water. The value  $m_t$  is obtained by adding the amounts of lithium extracted for the time  $t$  (Figure 4).

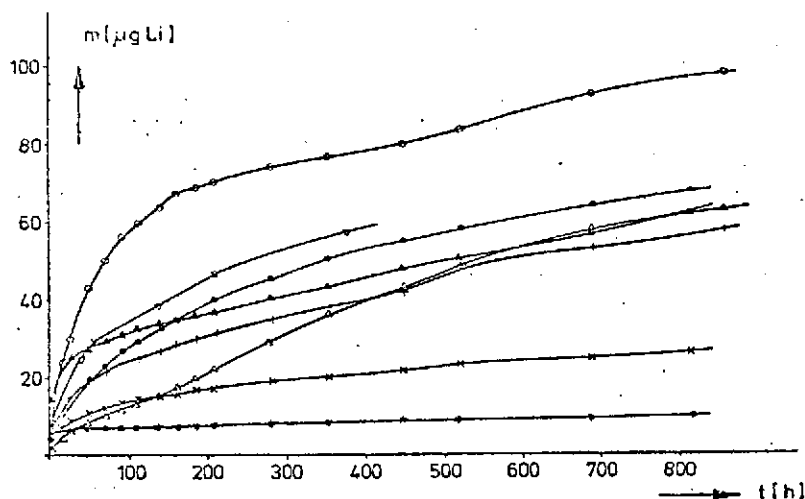


Figure 4. Time course of the extraction. (Explanation of symbols in Table 4).

Table 4. TIME COURSE OF THE EXTRACTION (SEE FIGURES 4 - 7) AND DIFFUSION COEFFICIENTS  $D_0$  and  $D_\infty$ .

Formulations	Symbols in Fig. 4-7	$D_0$	$D_\infty$
Vestolen A 6016* + 1 T. K30	□ ***	$3,0 \cdot 10^{-16}$	
Vestolen A 6016* + 1 T. K30	+ 1 T. Gl □	$7,8 \cdot 10^{-13}$	
Vestolen A 6016** + 1 T. K30	+ 1 T. Gl +	$2,1 \cdot 10^{-12}$	$8,1 \cdot 10^{-12}$
Vestolen A 6016* + 1 T. K30	+ 2 T. Gl ▽	$4,8 \cdot 10^{-12}$	
Vestolen A 6016** + 1 T. Marlon A	+ 1 T. Gl ○	$3,8 \cdot 10^{-12}$	$1,1 \cdot 10^{-11}$
Vestolen A 5017 + 1 T. K30	+ 1 T. Gl ×	$8,9 \cdot 10^{-13}$	$3,2 \cdot 10^{-12}$
Vestolen P 5500 + 2 T. K30	+ 1 T. Gl ○	$3,1 \cdot 10^{-12}$	$6,7 \cdot 10^{-12}$
Vestolen BT 8000 + 2 T. K30	+ 1 T. Gl Δ	$2,0 \cdot 10^{-12}$	$5,7 \cdot 10^{-12}$
Vestyron 512 + 2 T. K30	* ***	$2,8 \cdot 10^{-15}$	
Vestyron 512 + 2 T. K30	+ 1,5 T. Gl Δ ****	$1,2 \cdot 10^{-11}$	$3,9 \cdot 10^{-11}$

T: parts per hundred parts, by weight      Gl: glycerin

\*: Batch 1

\*\*: Batch 2

\*\*\*: Values too small for Figure 4

\*\*\*\*: Measurement  $\cdot 10^{-1}$  plotted in Figure 4

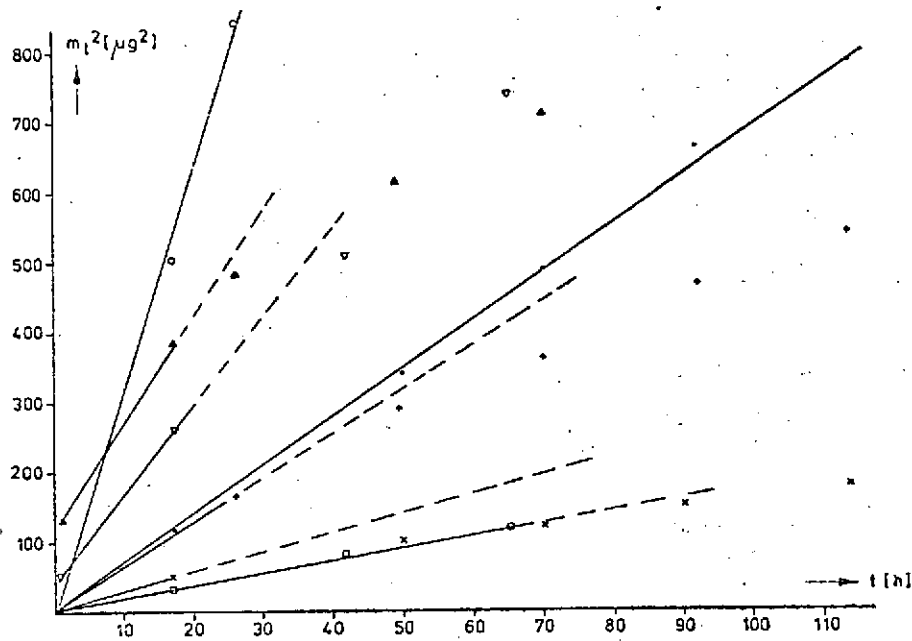


Figure 5. Time course of the extraction in the initial phase, quadratic plot.

In order to calculate the diffusion coefficients in the initial phase of the extraction ( $D_0$ ) we used the relation [45]:

$$D_0 = \frac{\pi \cdot a^2 \cdot \Delta m_t^2}{16 \cdot m_g^2 \cdot \Delta t}$$

in which  $a$  is the sheet thickness,  $m_t$  is the amount of lithium extracted at time  $t$ , and  $m_g$  is the total amount of lithium used. If we plot  $m_t^2$  versus  $t$  (Figures 5 and 6), then we can calculate the Diffusion coefficient  $D_0$  from the initial slope,  $S_0 = \frac{\Delta m_t^2}{\Delta t}$ :

$$D_0 = \frac{\pi \cdot a^2 \cdot S_0}{16 m_g^2}$$

The values obtained are shown in Table 4. For longer times, the change of concentration in the interior of the sheets must be

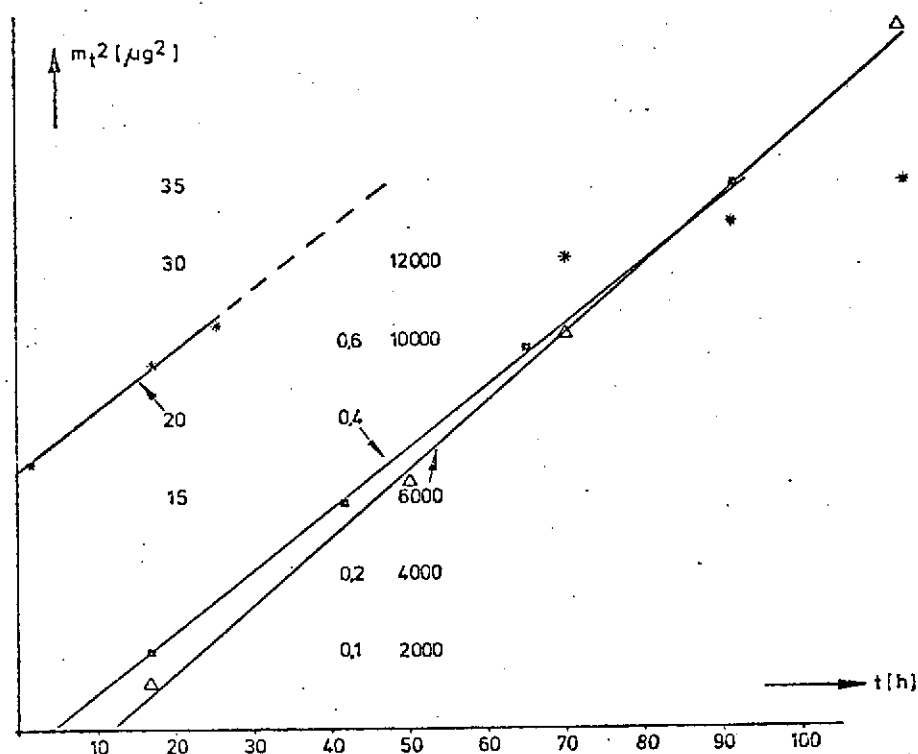


Figure 6. Time course of the extraction in the initial phase, quadratic plot.

taken into consideration. Then the proper equation is [45]:

$$D_{\infty} = - \frac{a^2 \cdot \Delta \ln \frac{m_g - m_t}{m_g}}{\pi^2 \cdot \Delta t}$$

Now if  $\log \frac{m_g - m_t}{m_g}$  is plotted versus  $t$ , we should also get straight lines for long times if Fick's Second Law holds (Figure 7).

Then, by inserting the slope,  $S_{\infty}$ , we can calculate the diffusion coefficient,  $D_{\infty}$ , according to the relation:

$$D_{\infty} = \frac{2.3 \cdot a^2 \cdot S_{\infty}}{\pi^2}$$

The values obtained are also shown in Table 4. Values were not calculated for  $D_{\infty}$  when the extraction times were too low or the amounts extracted were too small.

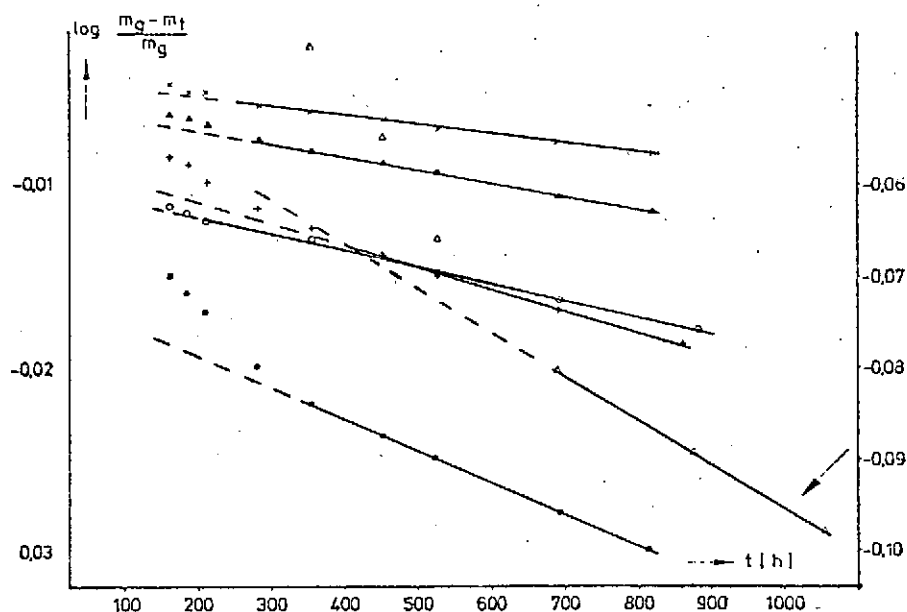


Figure 7. Time course of the extraction in the range of 200 to 1,000 hours after beginning, logarithmic plot.

In both cases, as Figure 4 shows, addition of glycerin produces an increase in the diffusion coefficients by a factor of  $3 - 4 \cdot 10^3$ . This is in conformance with the degree of surface coating for the same polymers and the same antistatic agents. The fact that  $D_0$  is somewhat smaller than  $D_\infty$  throughout indicates that only part of the incorporated lithium salt is available for diffusion [42]. As  $m_g$  decreases,  $D_0$  rises more rapidly than  $D_\infty$ .

For comparison with the values in Table 4 above, let us cite the diffusion coefficient for amines in polyethylene, which are known to exude easily. This is described in the literature [11] as  $1 - 2 \cdot 10^{-9}$ . If, in the preceding, the diffusion coefficient is used as a measure for the migration rate, one should always remember that this certainly does not describe the true conditions in the polymers. The processes at the phase boundaries will always exert an effect on the magnitude of the coefficients.

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## REFERENCES

- <sup>1</sup> Y. I. VASILENOK, A. S. DEVANOV, B. A. KONOPLEV, V. N. LAGUNOVA, S. H. I. LELCHUK und B. I. SAZHIN, *Soviet Plastics* 1970 [5] 49
- <sup>2</sup> W. T. M. JOHNSON, *Off. Dig. Fed. Soc. Paint Technol.* 32 (1960) 1067 und 33 (1961) 1489
- <sup>3</sup> H. MARUMO und M. TAKAI, *Kogyo Kagaku [J. Chem. Soc. Japan, Ind. Chem. Sect.]* 68 (1965) 2209
- <sup>4</sup> D. L. WOLFE (*Soc. Plast. Eng.*), 28. Tech. Pap. 1970, 721
- <sup>5</sup> S. BADIYESCU, M. TOADER und H. O. OPREA, *Mater. Plast. [Bucuresti]* 8 (1971) 422
- <sup>6</sup> A. E. SHEER und E. A. VITALIS, *Ind. Eng. Chem., Prod. Res. Develop.* 2 [2] (1963) 97
- <sup>7</sup> C. G. VOM BRUCK, K. FIGGE und V. WOLF, *Deut. Lebensm. Rundsch.* 66 (1970) 253
- <sup>8</sup> K. FIGGE und J. SCHOENE, *Deut. Lebensm. Rundsch.* 66 (1970) 281
- <sup>9</sup> K. FIGGE und H. PIATER, *Deut. Lebensm. Rundsch.* 67 (1971) 47, 110, 154, 235
- <sup>10</sup> K. FIGGE, *Kunststoffe* 61 (1971) 832
- <sup>11</sup> R. A. JACKSON, S. R. OLDELAND und A. PAJACZKOWSKI, *J. Appl. Polym. Sci.* 12 (1968) 1297
- <sup>12</sup> A. J. G. ALLAN, *J. Colloid Interface Sci.* 14 (1959) 206
- <sup>13</sup> H. MARUMO und M. TAKAI, *Yukagaku [J. Jap. Oil Chem. Soc.]* 14 (1965) 619
- <sup>14</sup> W. BIEDERMANN, G. LANGHAMMER und W. REICHERDT, *Plast. Kaut.* 19 (1972) 119
- <sup>15</sup> DT-OS 2005854 (10. 2. 1970/26. 8. 1971); Chem. Werke Hüls AG, Erf.: K. ROMBUSCH, F. SEIFERT, D. CARLA und U. EICHERS
- <sup>16</sup> DT-OS 2153438 (27. 10. 1971/3. 5. 1973); Chem. Werke Hüls AG, Erf.: K. ROMBUSCH, G. MAARS und U. EICHERS
- <sup>17</sup> P. SENN, *Dissertation Reutlingen-Stuttgart* 1955; Reyon, Zellwolle, andere Chemiefasern 8 (1958) 865
- <sup>18</sup> A. E. HENSHALL, *J. Soc. Dyers Colour.* 76 (1966) 525
- <sup>19</sup> C. YONESE, *Science [Japan]* 14 (1944) 389
- <sup>20</sup> W. C. GRIFFIN, R. W. BEHRENS und S. T. CROSS, *J. Soc. Cosmet. Chem.* 1952 [3] 5,
- <sup>21</sup> P. VÉLON, *Seifen-Öle-Fette-Wachse* 81 (1955) 89, 115
- <sup>22</sup> G. C. HENNEY, R. V. EVANSON und G. J. SPERANDIO, *J. Soc. Cosmet. Chem.* 9 (1958) 329
- <sup>23</sup> Z. V. UCHASTKINA, *Tr. Leningrad. Technol. Inst. im. V. M. Molotova* 1958 [5] 153
- <sup>24</sup> D. M. BRYCE und J. K. SUGDEN, *Pharmac. J.* 183 (1959) 311
- <sup>25</sup> H. v. CZETSCH-LINDENWALD und R. TAWASHI, *Am. Perfum. Cosmet., Toilet. Preparat.* 80 [9] (1965) 31
- <sup>26</sup> C. MARCU, M. POPESCU und I. SOLOMON, 4. Int. Koloristenkongr. Budapest 1962, 175
- <sup>27</sup> GB-PS 488945 (18. 7. 1938), Erf.: D. FINLAYSON und R. G. PERRY
- <sup>28</sup> US-PS 2809159 (18. 11. 1954/8. 10. 1957) Dexter Chem. Corp., Erf.: E. I. WELLES und S. M. EDELSTEIN
- <sup>29</sup> US-PS 3519561 (23. 6. 1966/7. 7. 1970), GAF Corp., Erf.: A. J. KELLY und R. C. BRITT
- <sup>30</sup> DT-OS 1619001 (13. 1. 1967/30. 7. 1970), Dow Corning Corp., Erf.: J. K. CAMPBELL
- <sup>31</sup> US-PS 3296020 (27. 8. 1964/3. 1. 1967), Bibb Manuf. Co., Erf.: R. F. SHEEHAN
- <sup>32</sup> CS-PS 135643 und 135650 (7. 12. 1966/15. 3. 1970), 136137 und 136140 (7. 12. 1966/1. 4. 1970), Erf.: J. VAHALA, J. JOZEFCEK und J. SPONAR
- <sup>33</sup> JA-PS 6700861 (16. 10. 1962/18. 1. 1967), Nippon Oils and Fats Co. Ltd., Erf.: K. KAMESAWA

- <sup>34</sup> JA-PS 6702071 (1. 3. 1963/30. 1. 1967), Tokyo Shibaura Electric Co., Erf.: Y. MIURA, T. TSUKADA und S. HAYASHI
  - <sup>35</sup> JA-PS 7013705 (30. 8. 1965/16. 5. 1970), Daiichi Kogyo Seiyaku Co. Ltd., Erf.: J. MORIGUSHI und N. KOBAYASHI
  - <sup>36</sup> US-PS 1570076 (16. 9. 1920/19. 1. 1926), E. I. Du Pont de Nemours und Co., Erf.: E. C. PITMAN
  - <sup>37</sup> DT-OS 2050770 (15. 10. 1970/22. 4. 1971), Uniroyal Inc., Erf.: G. D. BRINDELL und L. E. DANNALS
  - <sup>38</sup> US-PS 3361762 (27. 9. 1963/2. 1. 1968), Union Carbide Corp., Erf.: L. H. WARTMAN und C. E. ROTH, jr.
- 
- <sup>39</sup> H. NIEBERGALL, Kunststoffe 58 (1968) 242; Angew. Makromol. Chem. 18 (1971) 121
  - <sup>40</sup> H. NIEBERGALL und H. SEITZ, Angew. Makromol. Chem. 27 (1972) 129
  - <sup>41</sup> GB-PS 838161 (19. 9. 1958/24. 1. 1962), Commercial Plastic Ltd., Erf.: A. STERN und A. P. SMITH
  - <sup>42</sup> DT-AS 1215925 (12. 12. 1963/5. 5. 1966), Siemens Schuckertwerke AG, Erf.: G. BÜRKLIN und W. JOHN
  - <sup>43</sup> R. KREUTER, Seifen-Öle-Fette-Wachse 97 (1971) 255
  - <sup>44</sup> V. P. VOROB'EV, Z. G. GURICHEVA, L. I. PETROVA und B. I. SAZHIN, Soviet Plastics 1972 [7], 64
  - <sup>45</sup> u. a. in P. MEARES, Polymers, Structure and Bulk Properties, D. van Nostrand Co. Ltd., London 1965, S. 320